

## Indicator: Acid Deposition (011, 218, 032)

Every year, millions of tons of sulfur dioxide and nitrogen oxides are emitted to the atmosphere as a result of the burning of fossil fuels (EPA, 2003, p. 18). These gases react with water, oxygen, and oxidants to form acidic compounds, which may be carried hundreds of miles by the wind – even across state or national borders. Acid deposition occurs when these compounds fall to the Earth in one of two forms: wet (dissolved in rain, snow, and fog) or dry (solid and gaseous particles deposited on surfaces during periods of no precipitation). While wet deposition is the more widely recognized form (more commonly referred to as “acid rain”), dry deposition can account for 20 to 60 percent of total acid accumulation (EPA, 2001, p. 115).

In the environment, acid deposition causes soils and water bodies to acidify, which can make the water unsuitable for some fish and other wildlife. It also damages some trees, particularly at high elevations, and speeds the decay of buildings, statues, and sculptures that are part of our national heritage (EPA, 2003b, p. 18). The nitrogen portion of acid deposition also contributes to eutrophication in coastal ecosystems, the symptoms of which include potentially toxic algal blooms, fish kills, and loss of plant and animal diversity. Acidification of lakes and streams can increase the amount of methylmercury available in aquatic systems, which indicator 038 discusses further. Finally, increased levels of sulfate in ground-level air – a phenomenon related to dry deposition – can contribute to decreased visibility as well as a variety of human health problems (EPA, 2003b, p. 18).

Total acid deposition in this indicator is determined using both wet and dry deposition measurements. Wet deposition is measured through chemical analysis of rainwater collected at sites across the United States. The chemical components of wet deposition include sulfate, nitrate, and ammonium. Dry deposition is not measured directly. Rather, EPA measures ambient air concentrations of acidic compounds and then calculates deposition rates using a model that depends on meteorology and vegetative cover (<http://www.epa.gov/castnet/>.) Chemicals measured include components of particulate matter [sulfate ( $\text{SO}_4$ ) and nitrate ( $\text{NO}_3$ )], gaseous nitric acid ( $\text{HNO}_3$ ), sulfur dioxide ( $\text{SO}_2$ ), and ammonium ( $\text{NH}_4$ ). This indicator uses the three-year average from 1989-1991 as a baseline, as this period immediately predates controls on sulfur and nitrogen oxide emissions mandated by the 1990 Clean Air Act Amendments.

### What the Data Show

Analyses of long-term monitoring data from the National Atmospheric Deposition Program (NADP) show that *wet deposition* of both sulfur and nitrogen compounds has decreased over the last 15 years:

Wet sulfate deposition decreased significantly across much of the United States over the 1990s (Figure 011-1). The greatest reductions in wet sulfate deposition occurred in the Mid-Appalachian region (Maryland, New York, West Virginia, Virginia, and most of Pennsylvania) and the Ohio River Valley. Less dramatic reductions were observed across much of New England and portions of the Southern Appalachians. Average regional decreases in wet deposition of sulfate between the periods 1989-1991 and 2001-2003 were 39 percent in the Northeast, 36 percent in the Midwest, and 17 percent in the Southeast.

Concentrations of nitrate in precipitation decreased approximately 15 percent across the Northeast and Mid-Atlantic regions during the 1990s, but other areas did not show much change (Figure 011-2).

As with wet deposition, *total deposition* (the sum of wet and dry deposition) also decreased between 1989-1991 and 2001-2003, and reductions were more significant for sulfur compounds than for nitrogen compounds (figures 011-3 and 011-4).

## Indicator Limitations

- Geographic coverage is limited, particularly for dry deposition (and thus total deposition as well), but the concentration of sites in the Midwest and Northeast is justified by the fact that acid rain is much more of a problem in those regions than it is in the West, Great Plains, or Southeast.
- Measurement techniques for dry deposition have improved substantially, but characterization of dry deposition still requires a combination of measurements and modeling, which has inherent uncertainties.

## Data Sources

Wet deposition: EPA's National Acid Deposition Program (NADP): <http://nadp.sws.uiuc.edu/>. Dry deposition: EPA's Clean Air Status and Trends Network (CASTNet): <http://www.epa.gov/castnet/>.

## References

U.S. Environmental Protection Agency. 2003a. Latest Findings on National Air Quality: 2002 Status and Trends, EPA 454/K-03-001. Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of Air and Radiation, Office of Air Quality Planning and Standards, August 2003.  
[http://www.epa.gov/airtrends/2002\\_airtrends\\_final.pdf](http://www.epa.gov/airtrends/2002_airtrends_final.pdf).

U.S. Environmental Protection Agency. 2003b. National Air Quality and Emissions Trends Report, 2002, EPA 454/R-01-004. Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of Air and Radiation, Office of Air Quality Planning and Standards, August 2003.  
[http://www.epa.gov/airtrends/2002\\_airtrends\\_final.pdf](http://www.epa.gov/airtrends/2002_airtrends_final.pdf)

For a description of EPA's Acid Rain program, see <http://www.epa.gov/airmarkets/arp/index.html/> .

## Graphics

Figure OII-1: Wet sulfate deposition, 1989-1991 vs. 2001-2003

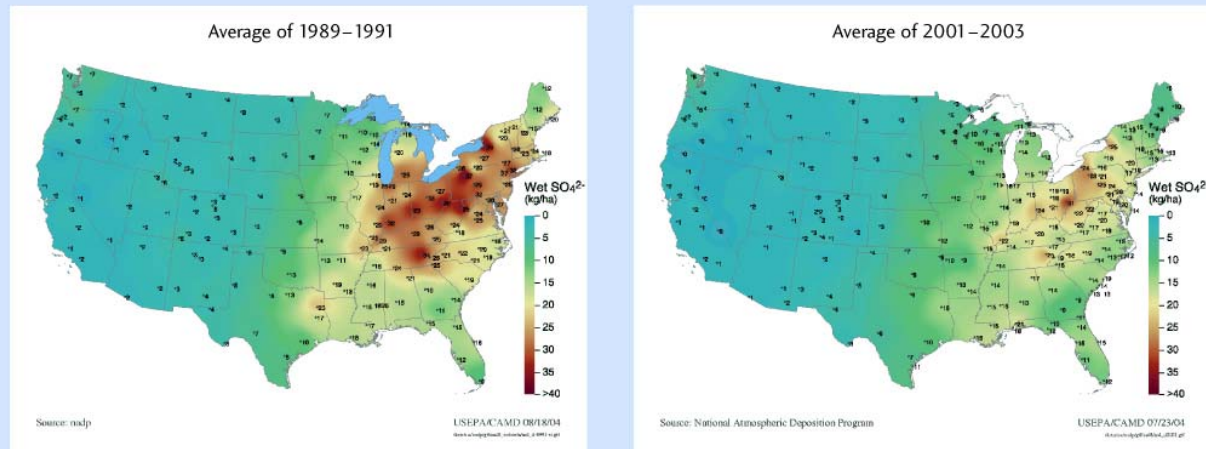


Figure OII-2: Wet nitrate deposition, 1989-1991 vs. 2001-2003

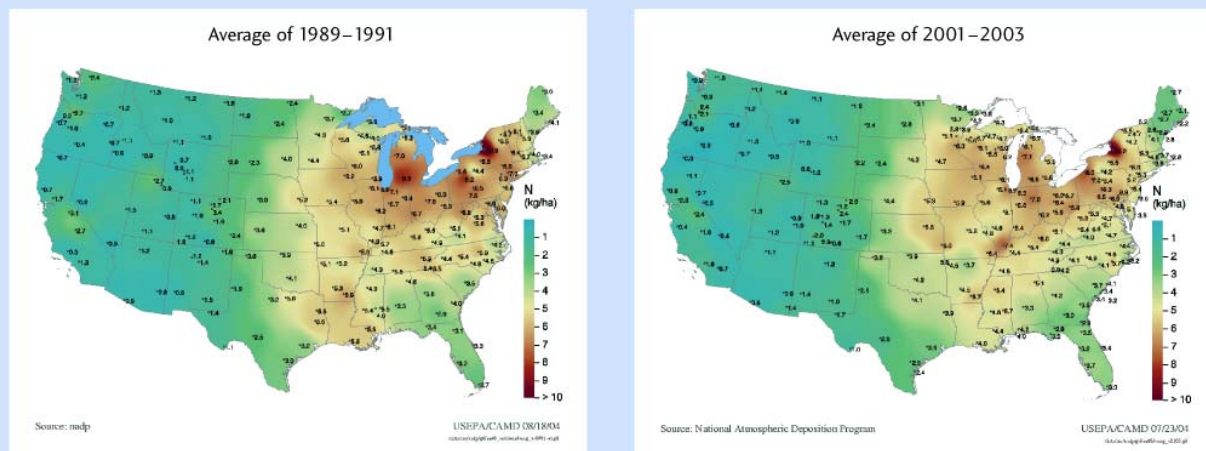


Figure OII-3: Total sulfur deposition, 1989-1991 vs. 2001-2003

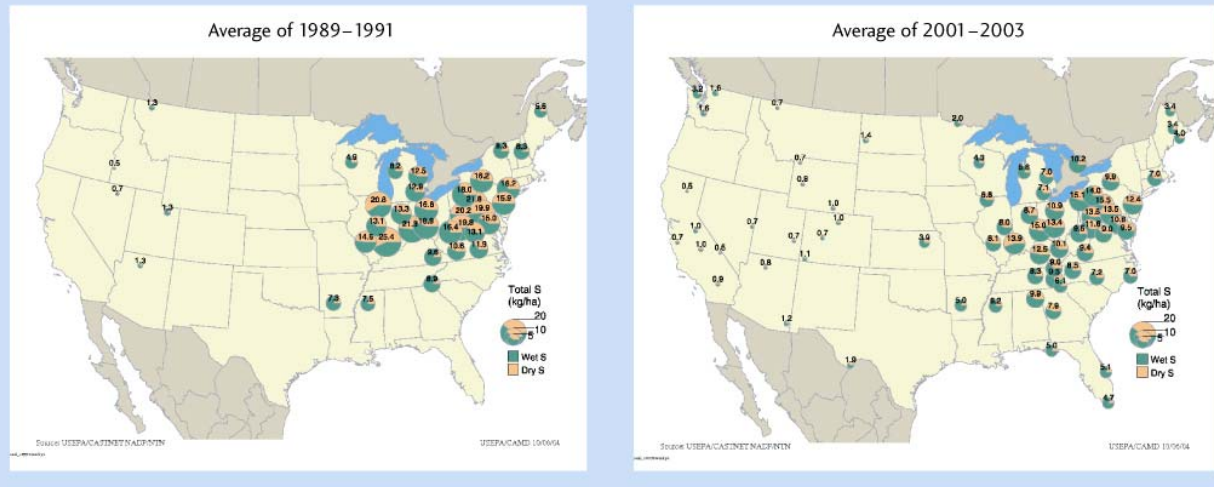
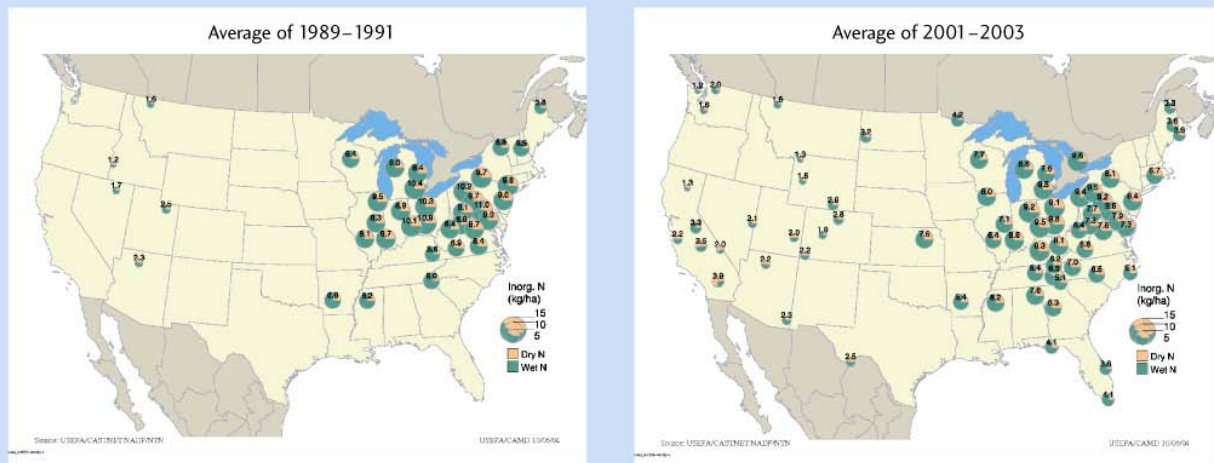


Figure OII-4: Total nitrogen deposition, 1989-1991 vs. 2001-2003



## R.O.E. Indicator QA/QC

**Data Set Name:** ACID DEPOSITION

**Indicator Number:** 011 (89083)

**Data Set Source:** CASTNet, see <http://www.epa.gov/castnet/> and for NADP, see <http://nadp.sws.uiuc.edu/>

**Data Collection Date:** ongoing:1989-1991, 2001-2003

**Data Collection Frequency:** hourly and weekly

**Data Set Description:** Acid Deposition (Wet Sulfate, Wet Nitrate, Total S, Total N)

**Primary ROE Question:** What are the trends in outdoor air quality and effects on human health and ecological systems?

### Question/Response

**T1Q1** Are the physical, chemical, or biological measurements upon which this indicator is based widely accepted as scientifically and technically valid?

Yes, both CASTNET and NADP measurements are widely accepted as scientifically and technically valid. Measurements and Sampling Methods: Each CASTNET site measures atmospheric sulfur and nitrogen pollutants (i.e. SO<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>, HNO<sub>3</sub>, NO, total Nitrate, NH<sub>4</sub>), cations (NA, K, MG, and Ca), and hourly measurements of meteorological conditions and supporting information on vegetation and land use. Concentrations of ambient sulfur and nitrogen species are collected and measured weekly via a 3-stage filter pack. In addition to sulfur and nitrogen, many CASTNET sites have hourly measurements of O<sub>3</sub> concentrations. Ambient O<sub>3</sub> concentrations are measured via ultraviolet (UV) absorbance. Measured meteorological variables and information on vegetation and land use are used as input into a Multilayer Resistance Model (MLM) to determine flux. NADP/NTN analyzes the constituents important in precipitation chemistry, including those affecting rainfall acidity and those that may have ecological effects. The NADP/NTN measures sulfate, nitrate, hydrogen ion (measure of acidity), ammonium, chloride, and base cations (calcium, magnesium, potassium). Each site has a precipitation chemistry collector and a rain gage (to determine the amount of precipitation) and samples are collected weekly. To ensure comparability of results, laboratory analyses for all samples are conducted by the NADP's Central Analytical Lab at the Illinois State Water Survey. References Methods: " CASTNET Quality Assurance Project Plan [http://www.epa.gov/CASTNET/library/qapp\\_v2/qapp\\_a-f.pdf](http://www.epa.gov/CASTNET/library/qapp_v2/qapp_a-f.pdf). " NADP/NTN Quality Assurance Plan <http://nadp.sws.uiuc.edu/QA/> CASTNET Bias and Uncertainty has been identified by the following: " Allegrini, I., DeSantis, F., DiPalo, V., Febo, A., Perrino, C., Possanzini, M., Liberti, A., 1987. Annular denuder method for sampling reactive gases and aerosols in the atmosphere. Science of the Total Environment 67, 1-16. " Harrison, R.M., Kitto, A.-M.N., 1990. Field intercomparison of filter pack and denuder sampling methods for reactive gaseous and particulate pollutants. Atmospheric Environment 24A, 2633-2640. " Sickles, J.E., II, Hodson, L.L., 1989. Fate of nitrous acid on selected collection surfaces. Atmospheric Environment 23, 2321-2324.



**T1Q2** Is the sampling design and/or monitoring plan used to collect the data over time and space based on sound scientific principles?

Yes, the sampling design and monitoring plan for CASTNET and NADP are based on sound scientific principles. Network Design: CASTNET network design involves the measurement of rural, regionally representative concentrations of sulfur and nitrogen species to estimate dry deposition fluxes and to assess trends over time and space. Eastern U.S. sites are selected based on regional representation (overall similarity of the site to a characteristic area), distance from major pollutant sources (i.e. located approximately 100 km from a pollutant emission source), long-term availability, accessibility, and good geographic coverage. However, for the western United States, the limited number of sites and higher diversity of the region makes it difficult to determine spatial patterns. Therefore, site selection in the West focuses primarily on locations where specific research issues can be addressed, and where natural resources are at risk (e.g., national parks). For more information, refer to CASTNET Quality Assurance Plan (QAPP), October 2003, available at [http://www.epa.gov/CASTNET/library/qapp\\_v2/qapp\\_a-f.pdf](http://www.epa.gov/CASTNET/library/qapp_v2/qapp_a-f.pdf) The NADP was initiated in the late 1970s as a cooperative program between federal and state agencies, universities, electric utilities, and other industries to determine geographical patterns and trends in precipitation chemistry in the United States. Monitoring sites for NADP networks are selected to represent major physiographic, agricultural, aquatic, and forested areas within states, regions or ecoregions. Sites are predominantly located away from urban areas and point sources of pollution. For more information, refer to the NADP Site Selection and Installation Manual available at <http://nadp.sws.uiuc.edu/lib/manuals/siteinst.pdf>.

**T1Q3** Is the conceptual model used to transform these measurements into an indicator widely accepted as a scientifically sound representation of the phenomenon it indicates?

Yes, the model used to estimate dry deposition from CASTNET data and the methods used to calculate wet deposition from NADP data are scientifically and technically valid. The MLM (Multi-Layer Model) is the mathematical model that simulates dry deposition processes using CASTNET data. Dry deposition (D) is a flux calculated from measured pollutant concentration (C) and a modeled Vd. Vd is calculated based on parameters such as meteorological conditions, vegetation, and land use, which are inputs to the MLM. For more detailed information on the MLM, refer the Clean Air Status and Trends Network Quality Assurance Plan (QAPP), October 2003, available at [http://www.epa.gov/CASTNET/library/qapp\\_v2/qapp\\_a-f.pdf](http://www.epa.gov/CASTNET/library/qapp_v2/qapp_a-f.pdf). For NADP/NTN, mean wet concentrations are precipitation-weighted averages. Wet deposition is calculated by multiplying precipitation-weighted mean concentrations by total precipitation. The NADP methods of determining wet deposition values have undergone extensive peer review. Assessments of changes in NADP methods are developed primarily through the academic community and reviewed through the technical literature process. For more information on sampling procedures and calculations, refer to the NADP/NTN Quality Assurance Plan <http://nadp.sws.uiuc.edu/QA/> References: The MLM has been evaluated by the following: " Meyers, T. P., Finkelstein, P., Clarke, J., Ellestad, T.G., and Sims, P.F. 1998. A Multilayer Model for Inferring Dry Deposition Using Standard

Meteorological Measurements. J. Geophys. Res., 103D17:22,645-22,661. " Finkelstein, P.L., Ellestad, T.G., Clarke, J.F., Meyers, T.P., Schwede, D.B., Hebert, E.O., and Neal, J.A. 2000. Ozone and Sulfur Dioxide Dry Deposition to Forests: Observations and Model Evaluation. JGR. 105:D12:15,365-15,377. " Clarke, J.F., Edgerton, E.S., Martin, B.E., 1997. Dry deposition calculations for the Clean Air Status and Trends Network. Atmospheric Environment 31, 3667-3678.

**T2Q1** To what extent is the indicator sampling design and monitoring plan appropriate for answering the relevant question in the ROE?

The sampling design and monitoring plan for CASTNET and NADP are appropriate for answering the relevant question in the ROE regarding acid deposition. CASTNET was designed to investigate the relationship between changes in emissions (resulting from national emissions control programs) and changes in atmospheric sulfur and nitrogen concentrations and dry deposition. The current network design satisfies CASTNET objectives and used in conjunction with NADP wet deposition measurements, enables EPA to assess trends in atmospheric sulfur and nitrogen concentrations and wet and dry deposition over space and time. Total deposition is calculated as the sum of dry and wet deposition estimated at each CASTNET site and nearby NADP sites. As of December 2004, 88 CASTNET sites were operational at 86 distinct locations. CASTNET long-term data set contains dry deposition estimates from 1987 to present, with the longest data records primarily at eastern sites. The sampling frequency for the filter packs is weekly, Tuesday to Tuesday (168 hours) and the data are averaged over the one week period (refer to Deposition Flux Calculations section D.4.2.1, CASTNET QAPP, October 2003 [http://www.epa.gov/castnet/library/qapp\\_v2.html](http://www.epa.gov/castnet/library/qapp_v2.html) for more information). Meteorological conditions are sampled continuously and averaged hourly. Currently, there are greater than 250 NADP/NTN sites across the U.S. Site descriptions and a site map are available at <http://nadp.sws.uiuc.edu/sites/ntnmap.asp>? Precipitation is collected weekly from NADP sites. The length of the data record varies based on site. The program began in 1978 and 114 sites have a data record extending back at least 20 years.

**T2Q2** To what extent does the sampling design represent sensitive populations or ecosystems?

Western CASTNET sites are primarily located in sensitive ecosystems and national parks. There are a large number of CASTNET sites in acid sensitive areas of the eastern U.S. For more information on sampling design, see question T1Q2. Similarly, NADP/NTN sites are located in acid-sensitive receptor areas and also selected to represent major physiographic, agricultural, aquatic, and forested areas within states, regions, or ecoregions (e.g. hydrologic regions).

**T2Q3** Are there established reference points, thresholds or ranges of values for this indicator that unambiguously reflect the state of the environment?

Through NADP and CASTNET long-term monitoring programs, for comparison purposes, EPA has established deposition baselines for both sulfur and nitrogen, which is the mean deposition value for the three year period from 1989 to 1991 (before Title IV).

**T3Q1** What documentation clearly and completely describes the underlying sampling and analytical procedures used?

The CASTNET Quality Assurance Plan (QAPP) [http://www.epa.gov/CASTNET/library/qapp\\_v2/qapp\\_a-f.pdf](http://www.epa.gov/CASTNET/library/qapp_v2/qapp_a-f.pdf) describes sampling and analytical procedures used. Additional CASTNET documentation, such as annual reports and quality assurance annual reports, are available on the web at <http://www.epa.gov/CASTNET/library.html>. For NADP, detailed information and documentation on the network design, data collection, QA procedures, etc are available on the web at <http://nadp.sws.uiuc.edu/lib/> and <http://nadp.sws.uiuc.edu/QA/>.

**T3Q2** Is the complete data set accessible, including metadata, data-dictionaries and embedded definitions or are there confidentiality issues that may limit accessibility to the complete data set?

CASTNET data are available on the CASTNET web site at <http://www.epa.gov/CASTNET/data.html>. CASTNET data are provided as ASCII comma-separated value (CSV) files compressed using PKZIP format. Documentation describing the content, format and codes of the data file is included in the compressed ZIP file. NADP data products, which include: weekly and daily precipitation chemistry data; monthly, seasonal, and annual precipitation-weighted mean concentrations; annual and seasonal wet deposition totals; daily precipitation totals, color isopleth maps of precipitation concentrations and wet deposition, and site information are available on the web at <http://nadp.sws.uiuc.edu/>.

**T3Q3** Are the descriptions of the study or survey design clear, complete and sufficient to enable the study or survey to be reproduced?

Yes, for CASTNET, the sampling design is clearly documented in the Quality Assurance Project Plan, October 2003, available at [http://www.epa.gov/CASTNET/library/qapp\\_v2/qapp\\_a-f.pdf](http://www.epa.gov/CASTNET/library/qapp_v2/qapp_a-f.pdf). Yes, for NADP/NTN, the Site Selection and Installation manual documents site selection procedures and the overall sampling strategy, available at <http://nadp.sws.uiuc.edu/lib/manuals/siteinst.pdf>

**T3Q4** To what extent are the procedures for quality assurance and quality control of the data documented and accessible?

CASTNET established a Quality Assurance Project Plan (QAPP) in November 2001. The QAPP is reviewed on a regular basis and updated to document any changes in quality assurance or operating procedures. The Clean Air Status and Trends Network Quality Assurance Plan and Quality Assurance Annual reports are available at <http://www.epa.gov/castnet/library.html>. NADP has established data quality objectives and quality control procedures for accuracy, precision and representation, available on the Internet: <http://nadp.sws.uiuc.edu/QA/>.



**T4Q1** Have appropriate statistical methods been used to generalize or portray data beyond the time or spatial locations where measurements were made (e.g., statistical survey inference, no generalization is possible)?

Yes, appropriate statistical methods have been used for spatial interpolation of wet and dry deposition, calculating annual annual average concentrations for CASTNET data, and calculating annual precipitation-weighted means for NADP data. For more information, refer to the CASTNET and NADP Quality Assurance Plans and Quality Assurance Annual reports, available at <http://www.epa.gov/castnet/library.html> and <http://nadp.sws.uiuc.edu/QA/>.

**T4Q2** Are uncertainty measurements or estimates available for the indicator and/or the underlying data set?

CASTNET has clearly defined Data Quality Objectives and Data Quality Indicators (DQI) for understanding the degree acceptability of the data collected. The DQI for CASTNET are precision, accuracy, bias, completeness, representativeness, and comparability. DQI are discussed in detail in Data Quality Objectives and Criteria, Section A.7, QAPP, October 2003. As there is no 'standard' network against which the NADP/NTN monitoring program can be measured, the network has attempted to estimate bias by comparing NADP/NTN data to those of other similar networks. The comparisons between the NADP/NTN Monitoring Network and Other Networks can be found at <http://nadp.sws.uiuc.edu/QA/intercomparisons.html>. NADP also has established data quality objectives and quality control procedures for accuracy, precision and representation, available on the Internet: <http://nadp.sws.uiuc.edu/QA/>.

**T4Q3** Do the uncertainty and variability impact the conclusions that can be inferred from the data and the utility of the indicator?

No, uncertainty and variability do not impact conclusions inferred from the data. For detailed information on uncertainty and variability, refer to the CASTNET and NADP Quality Assurance Plans and Quality Assurance Annual reports, available at <http://www.epa.gov/castnet/library.html> and <http://nadp.sws.uiuc.edu/QA/>.

**T4Q4** Are there limitations, or gaps in the data that may mislead a user about fundamental trends in the indicator over space or time period for which data are available?

In order to improve the spatial resolution of CASTNET and dry deposition modeling, additional monitoring sites are needed as CASTNET has no geographic coverage for the Midwest areas of the country and limited coverage in the Northwest. Also, total deposition estimates are based on point measurements and may not accurately depict regional deposition. All data gaps and limitations are clearly documented for users in CASTNET datasets. For NADP, there are no limitations or gaps in the data